

Applicants : Patrick Gane, Matthias Buri and Michael Kaessberger
Appl. No. : 10/532,475 (National Stage of PCT/IB2003/005082)
Filed : February 27, 2006

- R represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphtalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
- R' represents hydrogen or a hydrocarbon radical having from 1 to 40 carbon atoms,

and wherein said copolymer has an intrinsic viscosity less than or equal to 100 ml/g determined in accordance with the method known as the intrinsic viscosity method.

32. (New) The gloss activator according to claim 31, wherein q in formula (I) represents an integer such that $15 \leq (m+n+p)q \leq 120$.

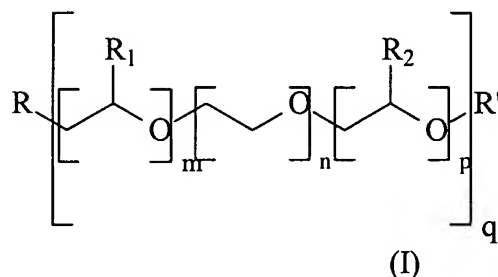
33. (New) The gloss activator according to claim 31, wherein R' in formula (I) represents a hydrocarbon radical having from 1 to 12 carbon atoms.

34. (New) The gloss activator according to claim 31, wherein R' in formula (I) represents a hydrocarbon radical having from 1 to 4 carbon atoms.

35. (New) The gloss activator according to claim 30, characterized in that said copolymer comprises:

- a) at least one anionic monomer with a carboxyl or dicarboxyl or sulfonic or phosphoric or phosphonic function or a mixture thereof,
- b) at least one non-ionic monomer, the non-ionic monomer comprising at least one monomer of formula (I):

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where

- m and p represent a number of alkylene oxide units less than or equal to 150,
 - n represents a number of ethylene oxide units less than or equal to 150,
 - q represents an integer equal to at least 1 and such that $5 \leq (m+n+p)q \leq 150$,
 - R_1 represents hydrogen or the methyl or ethyl radical,
 - R_2 represents hydrogen or the methyl or ethyl radical,
 - R represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphtalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides, and
 - R' represents hydrogen or a hydrocarbon radical having from 1 to 40 carbon atoms, or a mixture of several monomers of formula (I),
- c) at least one monomer of the acrylamide or methacrylamide type or their derivatives such as N-[3-(dimethylamino) propyl] acrylamide or N-[3-(dimethylamino) propyl] methacrylamide, and their mixtures, or at least one non water-soluble monomer such as the alkyl acrylates or methacrylates, unsaturated esters such as N-[2-(dimethylamino) ethyl] methacrylate, or N-[2-(dimethylamino) ethyl] acrylate, vinyls such as vinyl acetate, vinylpyrrolidone, styrene,

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alphamethylstyrene and their derivatives, or at least one cationic monomer or quaternary ammonium such as [2-(methacryloyloxy) ethyl] trimethyl ammonium chloride or sulphate, [2-(acryloyloxy) ethyl] trimethyl ammonium chloride or sulphate, [3-(acrylamido) propyl] trimethyl ammonium chloride or sulphate, dimethyl diallyl ammonium chloride or sulphate, [3-(methacrylamido) propyl] trimethyl ammonium chloride or sulphate, or at least one organofluorinated or organosilylated monomer, or a mixture of several of these monomers,

d) at least one monomer having at least two ethylenic insaturations referred to as a crosslinking monomer,

the total of the proportions of components a), b), c) and d) being equal to 100%,

and wherein said copolymer has an intrinsic viscosity less than or equal to 100 ml/g determined in accordance with the method known as the intrinsic viscosity method.

36. The gloss activator according to claim 35, wherein q in formula (I) represents an integer such that $15 \leq (m+n+p)q \leq 120$.

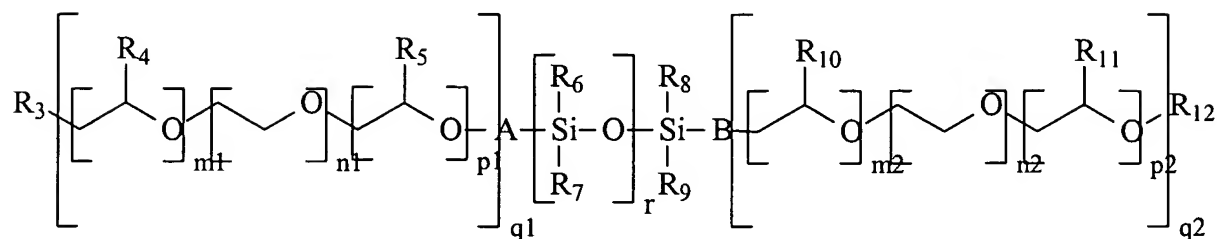
37. (New) The gloss activator according to claim 35, wherein R' in formula (I) represents a hydrocarbon radical having from 1 to 12 carbon atoms.

38. (New) The gloss activator according to claim 35, wherein R' in formula (I) represents a hydrocarbon radical having from 1 to 4 carbon atoms.

39. (New) The gloss activator according to claim 30, wherein the organosilylated monomer is selected from among the molecules of formulae (IIa) or (IIb),

with formula (IIa):

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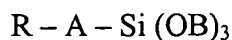


where

- m1, p1, m2 and p2 represent a number of alkylene oxide units less than or equal to 150
- n1 and n2 represent a number of ethylene oxide units less than or equal to 150
- q1 and q2 represent an integer equal to at least 1 and such that $0 \leq (m1+n1+p1)q1 \leq 150$ and $0 \leq (m2+n2+p2)q2 \leq 150$,
- r represents a number such that $1 \leq r \leq 200$,
- R₃ represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
- R₄, R₅, R₁₀ and R₁₁ represent hydrogen or the methyl or ethyl radical
- R₆, R₇, R₈ and R₉ represent straight or branched alkyl, aryl, alkylaryl or arylalkyl groups having from 1 to 20 carbon atoms, or a mixture thereof
- R₁₂ represents a hydrocarbon radical having from 1 to 40 carbon atoms,
- A and B are groups which may be present, in which case they represent a hydrocarbon radical having from 1 to 4 carbon atoms.

with formula (IIb)

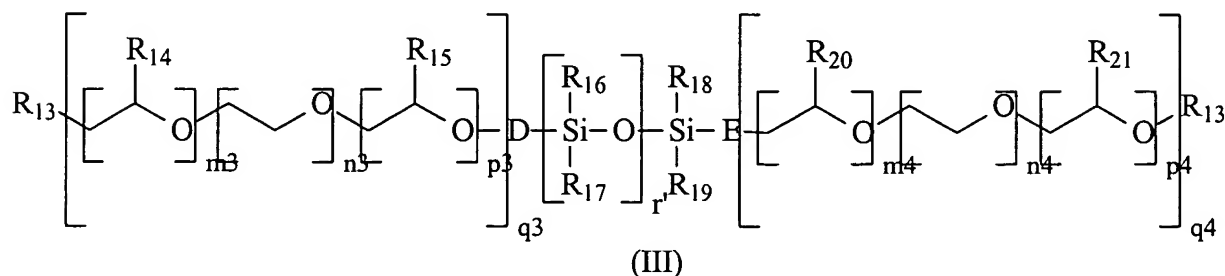
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where

- R represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
 - A is a group which may be present, in which case it represents a hydrocarbon radical having from 1 to 4 carbon atoms,
 - B represents a hydrocarbon radical having from 1 to 4 carbon atoms,
- or a mixture of several of said monomers,

and in that the crosslinking monomer is selected from the group consisting of ethylene glycol dimethacrylate, trimethylolpropanetriacrylate, allyl acrylate, the allyl maleates, methylene-bis-acrylamide, methylene-bis-methacrylamide, tetraallyloxyethane, triallylcyanurates, allyl ethers prepared from polyols such as pentaerythritol, sorbitol, sucrose, or selected from among the molecules of formula (III):



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where

- m₃, p₃, m₄ and p₄ represent a number of alkylene oxide units less than or equal to 150
 - n₃ and n₄ represent a number of ethylene oxide units less than or equal to 150
 - q₃ and q₄ represent an integer equal to at least 1 and such that $0 \leq (m_3+n_3+p_3)q_3 \leq 150$ and $0 \leq (m_4+n_4+p_4)q_4 \leq 150$,
 - r' represents a number such that $1 \leq r' \leq 200$,
 - R₁₃ represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
 - R₁₄, R₁₅, R₂₀ and R₂₁ represent hydrogen or the methyl or ethyl radical
 - R₁₆, R₁₇, R₁₈ and R₁₉ represent straight or branched alkyl, aryl, alkylaryl or arylalkyl groups having from 1 to 20 carbon atoms, or a mixture thereof
 - D and E are groups which may be present, in which case they represent a hydrocarbon radical having from 1 to 4 carbon atoms,
- or a mixture of several of said monomers.

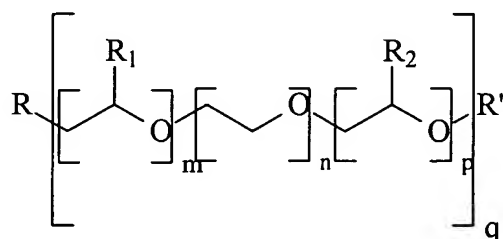
40. (New) The gloss activator of claim 30, wherein the copolymer comprises, by weight:

a) from 2% to 95% of at least one ethylenically unsaturated anionic monomer having a monocarboxyl function selected from among the ethylenically unsaturated monomers having a monocarboxyl function such as acrylic or methacrylic acid or hemiesters of diacids such as C₁ to C₄ monoesters of maleic or itaconic acid, or mixtures thereof, or having a dicarboxyl function selected from among the ethylenically unsaturated monomers having a dicarboxyl function such as crotonic, isocrotonic, cinnamic, itaconic, maleic acid, or anhydrides of carboxyl acids, such as maleic

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anhydride or having a sulfonic function selected from among the ethylenically unsaturated monomers having a sulfonic function such as acrylamido-methyl-propane-sulfonic acid, sodium methallylsulfonate, vinylsulfonic acid and styrenesulfonic acid or having a phosphoric function selected from among the ethylenically unsaturated monomers having a phosphoric function such as vinylphosphoric acid, ethylene glycol methacrylate phosphate, propylene glycol methacrylate phosphate, ethylene glycol acrylate phosphate, propylene glycol acrylate phosphate and their ethoxylates or having a phosphonic function selected from among the ethylenically unsaturated monomers having a phosphonic function such as vinylphosphonic acid, or mixtures thereof,

a) from 2 to 95% of at least one non-ionic ethylenically unsaturated monomer of formula (I):



(I)

where

- m and p represent a number of alkylene oxide units less than or equal to 150,
- n represents a number of ethylene oxide units less than or equal to 150,
- q represents an integer equal to at least 1 and such that $5 \leq (m+n+p)q \leq 150$,
- R₁ represents hydrogen or the methyl or ethyl radical,
- R₂ represents hydrogen or the methyl or ethyl radical,
- R represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane,

•

c) from 0% to 50% of at least one monomer of the acrylamide or methacrylamide type or their derivatives such as N-[3-(dimethylamino) propyl] acrylamide or N-[3-(dimethylamino) propyl] methacrylamide, and their mixtures, or at least one non water-soluble monomer such as the alkyl acrylates or methacrylates, unsaturated esters such as N-[2-(dimethylamino) ethyl] methacrylate, or N-[2-(dimethylamino) ethyl] acrylate, vinyls such as vinyl acetate, vinylpyrrolidone, styrene, aliphathylstyrene and their derivatives, or at least one cationic monomer or quaternary ammonium such as [2-(methacryloyloxy) ethyl] trimethyl ammonium chloride or sulphate, [2-(acryloyloxy) ethyl] trimethyl ammonium chloride or sulphate, [3-(acrylamido) propyl] trimethyl ammonium chloride or sulphate, dimethyl diallyl ammonium chloride or sulphate, [3-(methacrylamido) propyl] trimethyl ammonium chloride or sulphate, or at least one organofluorinated or at least one organosilylated monomer, selected preferably from among molecules of formulae (IIa) or (IIb),

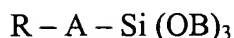
$$\left[\text{R}_3 - \left[\begin{array}{c} \text{R}_4 \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{n1} - \left[\begin{array}{c} \text{R}_5 \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{n1} - \left[\begin{array}{c} \text{R}_5 \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{p1} \right]_{q1} - \left[\begin{array}{c} \text{R}_6 \\ | \\ \text{---} \text{Si} \text{---} \text{O} \text{---} \\ | \\ \text{R}_7 \end{array} \right]_{r} - \left[\begin{array}{c} \text{R}_8 \\ | \\ \text{---} \text{Si} \text{---} \text{O} \text{---} \\ | \\ \text{R}_9 \end{array} \right]_{r} - \left[\begin{array}{c} \text{R}_{10} \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{m2} - \left[\begin{array}{c} \text{R}_{11} \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{n2} - \left[\begin{array}{c} \text{R}_{11} \\ | \\ \text{---} \text{CH} \text{---} \text{O} \text{---} \end{array} \right]_{p2} \right]_{q2} \text{R}_{12}$$

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where

- m_1, p_1, m_2 and p_2 represent a number of alkylene oxide units less than or equal to 150
- n_1 and n_2 represent a number of ethylene oxide units less than or equal to 150
- q_1 and q_2 represent an integer equal to at least 1 and such that $0 \leq (m_1+n_1+p_1)q_1 \leq 150$ and $0 \leq (m_2+n_2+p_2)q_2 \leq 150$,
- r represents a number such that $1 \leq r \leq 200$,
- R_3 represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
- R_4, R_5, R_{10} and R_{11} represent hydrogen or the methyl or ethyl radical
- R_6, R_7, R_8 and R_9 represent straight or branched alkyl, aryl, alkylaryl or arylalkyl groups having from 1 to 20 carbon atoms, or a mixture thereof
- R_{12} represents a hydrocarbon radical having from 1 to 40 carbon atoms,
- A and B are groups which may be present, in which case they represent a hydrocarbon radical having from 1 to 4 carbon atoms,

with formula (IIb)



where

- R represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane,

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- R₁₃ represents a radical containing a polymerizable unsaturated function, belonging to the vinyl group and to the group of acrylic, methacrylic, maleic, itaconic, crotonic, and vinylphthalic esters and to the group of urethane unsaturates such as acrylurethane, methacrylurethane, α - α' dimethyl-isopropenyl-benzylurethane and allylurethane, and to the group of allyl or vinyl ethers, whether or not substituted, or to the group of ethylenically unsaturated amides or imides,
 - R₁₄, R₁₅, R₂₀ and R₂₁ represent hydrogen or the methyl or ethyl radical
 - R₁₆, R₁₇, R₁₈ and R₁₉ represent straight or branched alkyl, aryl, alkylaryl or arylalkyl groups having from 1 to 20 carbon atoms, or a mixture thereof
 - D and E are groups which may be present, in which case they represent a hydrocarbon radical having from 1 to 4 carbon atoms,
- or a mixture of several of said monomers,

the total of the proportions of components a), b), c) and d) being equal to 100%,

and wherein the copolymer has intrinsic viscosity less than or equal to 100 ml/g determined in accordance with the method known as the intrinsic viscosity method.

41. (New) The gloss activator according to claim 40, wherein said copolymer comprises from 5% to 90% of component a).

42. (New) The gloss activator according to claim 40, wherein said copolymer comprises from 5% to 90% of component b).

43. (New) The gloss activator according to claim 40, wherein q in formula (I) represents an integer such that $15 \leq (m+n+p)q \leq 120$.

44. (New) The gloss activator according to claim 40, wherein R' in formula (I) represent a hydrocarbon radical having from 1 to 12 carbon atoms.

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45. (New) The gloss activator according to claim 40, wherein R' in formula (I) represent a hydrocarbon radical having from 1 to 4 carbon atoms.

46. (New) The gloss activator according to claim 30, characterized in that said copolymer is in its acid form or fully or partially neutralized by one or more neutralizing agents having a monovalent neutralizing function or a polyvalent neutralizing function such as, for the monovalent function, those selected from among the group consisting of the alkaline cations, in particular sodium, potassium, lithium, ammonium or the primary, secondary or tertiary aliphatic and/or cyclic amines such as stearylamine, the ethanolamines (mono-, di-, triethanolamine), mono and diethylamine, cyclohexylamine, methylcyclohexylamine, aminomethylpropanol, morpholine or, for the polyvalent function, those selected from among the group consisting of alkaline earth divalent cations, in particular magnesium and calcium, or zinc, and of the trivalent cations, including in particular aluminium, or of certain cations of higher valency.

47. (New) The gloss activator of claim 30, wherein said copolymer has an intrinsic viscosity less than or equal to 100 ml/g determined in accordance with the method known as the intrinsic viscosity method.

48. (New) A method for dispersing an aqueous suspension of mineral matter comprising the step of dispersing the mineral matter in the presence of the gloss activator according to claim 30.

49. (New) The method according to claim 48, wherein said copolymer comprises 0.05% to 5% by dry weight with respect to the dry weight of the fillers and/or pigments.

50. (New) The method according to claim 48, wherein said copolymer comprises 0.1% to 2.5% by dry weight with respect to the dry weight of the fillers and/or pigments.

51. (New) The method according to claim 48, characterized in that the mineral matter is selected from among calcium carbonate, dolomites, kaolin, calcine kaolin, talc, gypsum, titanium

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oxide, satin white or aluminium trihydroxide, mica and the mixture of these fillers, such as talc-calcium carbonate or calcium carbonate-kaolin mixtures, or mixtures of calcium carbonate with aluminium trihydroxide, or mixtures with synthetic or natural fibres or co-structures of minerals such as talc-calcium carbonate or talc-titanium dioxide co-structures.

52. (New) The method according to claim 48, characterized in that the mineral matter is calcium carbonate selected from marble, calcite, chalk or their mixtures.

53. (New) An aqueous suspension of mineral matter comprising the gloss activator according to Claim 30.

54. (New) The aqueous suspension of mineral matter according to claim 53, characterized in that it contains from 0.05% to 5% of said copolymer by dry weight with respect to the dry weight of mineral matter.

55. (New) The aqueous suspension of mineral matter according to claim 53, characterized in that it contains from 0.1% to 2.5% of said copolymer by dry weight with respect to the dry weight of mineral matter.

56. (New) The aqueous suspension of mineral matter according to claim 53, characterized in that the mineral matter is selected from among calcium carbonate, dolomites, kaolin, calcine kaolin, talc, gypsum, titanium oxide, satin white or aluminium trihydroxide, mica and the mixture of these fillers, such as talc-calcium carbonate or calcium carbonate-kaolin mixtures, or mixtures of calcium carbonate with aluminium trihydroxide, or mixtures with synthetic or natural fibres or co-structures of minerals such as talc-calcium carbonate or talc-titanium dioxide co-structures

57. (New) The aqueous suspension of mineral matter according to claim 53, characterized in that the mineral matter is calcium carbonate selected from marble, calcite, chalk or their mixtures.

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58. (New) A method for grinding an aqueous suspension of mineral matter comprising the step of grinding the aqueous suspension of mineral matter in the presence of the gloss activator according to claim 30.

59. (New) The method according to claim 58, characterized in that it contains from 0.05% to 5% by dry weight of said copolymer with respect to the dry weight of the fillers and/or pigments.

60. (New) The method according to claim 58, characterized in that it contains from 0.1% to 2.5% by dry weight of said copolymer with respect to the dry weight of the fillers and/or pigments.

61. (New) The method according to claim 58, characterized in that the mineral matter is selected from among calcium carbonate, dolomites, kaolin, calcine kaolin, talc, gypsum, titanium oxide, satin white or aluminium trihydroxide, mica and the mixture of these fillers, such as talc-calcium carbonate or calcium carbonate-kaolin mixtures, or mixtures of calcium carbonate with aluminium trihydroxide, or mixtures with synthetic or natural fibres or co-structures of minerals such as talc-calcium carbonate or talc-titanium dioxide co-structures.

62. (New) The aqueous suspension of mineral matter according to claim 58, characterized in that the mineral matter is calcium carbonate selected from marble, calcite, chalk or their mixtures.

63. (New) The aqueous suspension according to claim 58, wherein the mineral matter is ground mineral matter.

64. (New) Paper comprising a pigment prepared from the aqueous suspension of mineral matter according to claim 53, wherein the pigment is included in the coating or surface treatment of the paper.

65. (New) Paint comprising a pigment prepared from the aqueous suspension of mineral matter according to claim 53.

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66. (New) Plastic comprising a pigment prepared from the aqueous suspension of mineral matter according to claim 53.

67. (New) A coating colour prepared from the gloss activator according to claim 30.

68. (New) The coating colour according to claim 67, characterized in that it contains 0.05% to 5% of said copolymer by dry weight with respect to the dry weight of the mineral matter.

69. (New) The coating colour according to claim 67, characterized in that it contains 0.1% to 2.5% of said copolymer by dry weight with respect to the dry weight of mineral matter.

70. (New) Paper comprising the gloss activator of claim 30.

71. (New) Paint comprising the gloss activator of claim 30.

72. (New) Plastic comprising the gloss activator of claim 30.